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ESTIMATION OF HALOGENS IN ORGANIC COMPOUNDS

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INTRODUCTION

The method of estimation of halogens in organic compounds [1] consists in oxidising the substance with fuming nitric acid in a sealed tube under pressure in the presence of silver nitrate crystals. The silver halide formed is then filtered and weighed. The existing design is modified such that explosion hazard is minimised by this technique.

Requisites for the method

1. A thick walled (0.24 cm) soft glass tubing 60 to 62 cm long and 1.34 cm diameter rounded off at one end thoroughly cleaned with chromic acid, washed with distilled water and dried (Fig. 1A).

2. An ignition tube of 8.5 cm length and 0.6 cm diameter to contain the substance (Fig. 1B).

3. A thistle funnel with a long stem for introducing the nitric acid.

4. Pure fuming nitric acid free from halogen. This may be tested by diluting the nitric acid and adding a few drops of silver nitrate solution. The liquid should remain perfectly clear.

5. Pure silver nitrate crystals (AR).

6. Bomb furnace (Fig. 1C): This consists of a G.I. tube with one end closed and other end provided with a threaded lid as shown in the figure with provision for 2 holes for probing the temperature inside with dimensions as shown (Fig. 1C). The whole tube is wrapped with a heating tape of 250 watts capacity. Before starting the experiment the bomb furnace temperature was calibrated against a pyrometer for which a mercury thermometer was inserted in one hole and thermocouple of the pyrometer through the other.

Filling and selling the tube

About 0.1 to 0.2 gm of the finely powdered and dry substance was weighed accurately into the ignition tube. One gram of powdered silver nitrate crystals was introduced into the tube through the thistle funnel followed by one ml fuming nitric acid. The tube containing the substance was slipped gently so that the substance did not come into contact with acid. The open end of the tube was sealed in a blowpipe flame holding the tube upright.

When cold, the tube with contents was put inside the bomb furnace keeping the drawn-out capillary projecting. After closing the open end of the furnace with threaded lid the thermocouple of the pyrometer was inserted in one of the holes and the holes were kept in upright position so that if any explosion occurs the glass pieces may not face the operator. After switching on the furnace the temperature was raised gradually and kept within $150^\circ - 200^\circ$C for about $3-4$ hours and then at 250°C for another $2-3$ hours (the temperature can be controlled by putting the heating elements through a dimmerstat control). The experiment was started by morning and completed by evening and then the tube was allowed to cool overnight.

Opening of the sealed tube

The tube with capillary portion projecting out of the iron casing was heated in a flame so that the pressure due to nitrous fumes blows out and escapes. On no account the glass tube should be taken out before the above operation. When the pressure inside and outside the tube are the same, it can be safely taken out and the top drawn-out portion can be cut by suitable techniques (File mark can be made and cut or hot wire can be used for cutting). Bits of glass if any adhering to the sides near the open end are carefully removed. The contents of the tube containing the silver halide were now diluted by adding a few millilitres of water and then washed thoroughly into a beaker. The mixture was heated to boiling and the silver halide was filtered into a weighed sintered glass crucible (G4), washed with hot water containing a little nitric acid till free from silver nitrate, dried at $140-150^\circ$C and weighed.

Calculation

$$\frac{\text{At. wt. of halogen x wt. of silver halide}}{\text{m. wt. of silver halide}}$$

= wt. of halogen.

The above method was used for estimating halogen present in some compounds which were halogenated anodically in this laboratory.

Example for eosine (tetrabromofluorescein) or TBF

Atomic wt. of bromine	79.916
Wt. of silver bromide	0.1268 g
Wt. of substance taken	0.1092 g
Molecular weight of AgBr	187.8
Molecular weight of TBF	647.66

$$\text{Wt. of bromine} = \frac{79.916 \times 0.1268}{187.8}$$

$$= 0.05396 \text{ g}$$

647.66 g TBF = 79.916 x 4 g bromine

$$\text{Therefore } 0.1092 \text{ g TBF} = \frac{79.916 \times 4 \times 0.1092}{647.7}$$

$$= 0.5391 \text{ g}$$

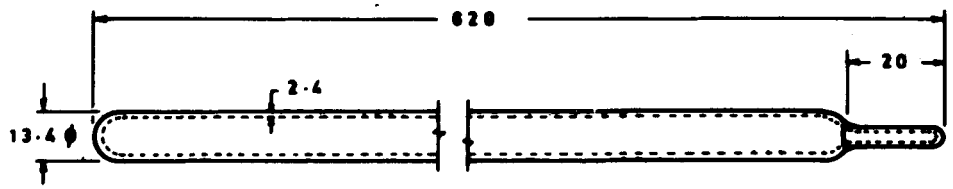

FIG. A.

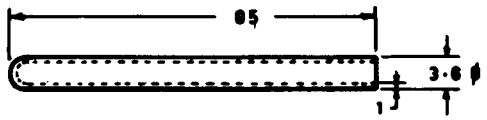

FIG. B.

* ALL DIMENSIONS ARE IN mm.

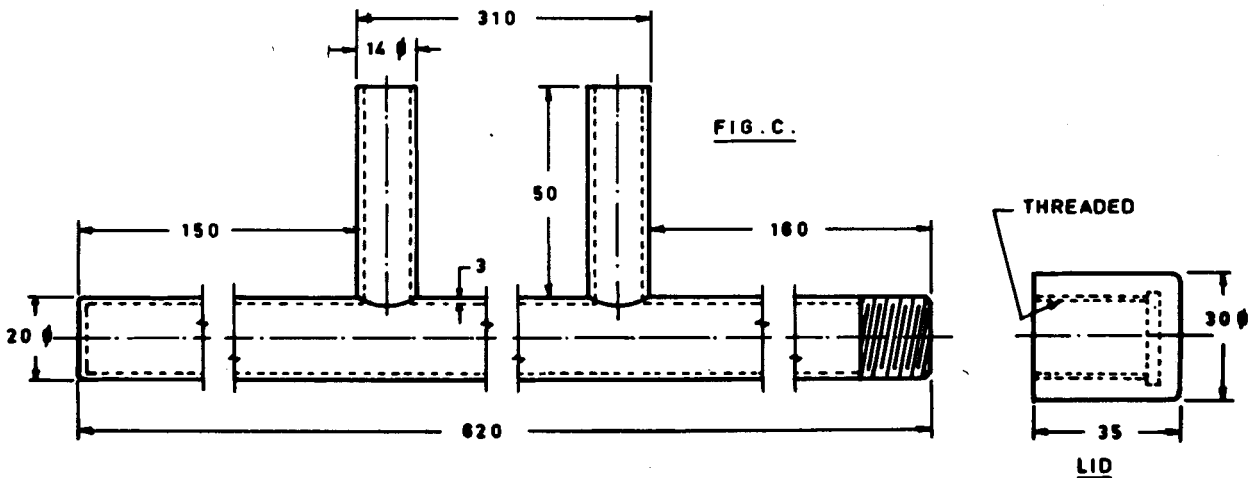

FIG. C.

Difference = $\begin{array}{l} 0.05396 - \\ 0.05391 \\ \hline 0.00005 \end{array}$

$$= \frac{0.00005 \times 100}{0.05396} = 0.09\%$$

2. Example for erythrosine (tetraiodofluorescein) or TIF

Atomic wt. of iodine	126.9
Wt. of silver iodide	0.212 g
Wt. of substance taken	0.1876 g
Molecular weight of AgI	234.8
Molecular weight of TIF	836.0

$$\text{Wt of iodine} = \frac{126.9 \times 0.212}{234.8}$$

$$= 0.1146 \text{ g}$$

836.0 g of TIF = 126.9 x 4 g iodine

$$\text{Therefore 0.1876 g of TIF} = \frac{126.9 \times 4 \times 0.1876}{836}$$

Difference = $\begin{array}{l} 0.1146 - \\ 0.1139 \\ \hline 0.0007 \end{array}$ = 0.1139 g

$$\frac{0.0007 \times 100}{0.1146} = 0.6\%$$

Acknowledgement

Thanks are due to Sri E Jagannathan, Lecturer, A.C. College of Engineering & Technology, Karaikudi for providing the experimental data for eosin and erythrosine who used this apparatus for his investigations.

REFERENCE

1. B B Dey and M V Sitaraman, *Laboratory Manual of Organic Chemistry*, S Viswanathan, Madras (1957) p. 387